Asbestos as a Solid Support in Gas Liquid Chromatography

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As an analytical technique, gas liquid chromatography is finding increasing use in both industry and research. The solid supports currently used for preparing the chromatographic columns are diatomaceous earths which besides being costly are not freely available. The possibility of using columns made from asbestos, a non-diatomaceous material, has been investigated. The performance of asbestos columns has been found to be superior to that of sterchamol columns and comparable to that of celite-545 columns.

THE diatomite earths are the most common solid supports employed in gas liquid chromatography. Chromosorbs P, W, G, Celite 545, Sil-O-Cel C-22, sterchamol, Gas Chrome S, G.C. super support, Porovina and Ryosorb are examples of this category[1-4]. Such solid supports are derived from diatomite filter aids or diatomite firebrick. Among the non-diatomite supports, the fluorocarbons, such as Teflon, Chromosorb T, Haloport F, Columpak T, Fluoropak 80 and Kel-F are the ones most widely used[4]. Other non-diatomite solid supports less commonly used are glass and nichrome beads, sand, carborundum, unglazed tile, Mipor No. 14PN-G, Tide (a detergent), sodium chloride and stannic phosphate[4]. The use of silver nitrate[5], Embacel[6], lyophilized solution of hexametaphosphate, sodium silicate and sodium sulphate[7], modified glass beads[8], teflon resin[9], coated molecular sieve[10], Aerogel[11] and Porapak[12] columns has also been recommended in gas liquid chromatography. The object of this study was to evaluate the suitability of asbestos, which is a diatomite filter aid, as a solid support in gas liquid chromatography.

Experimental procedure

Apparatus and materials — Chromatographic measurements were made with Willy Giede-gas chromatograph GCHF-18·3 equipped with a thermal conductivity detector. Stainless steel columns (1, 2 and 3 m long, int. diam. 4 mm) were used. Nitrogen was used as the carrier gas and the gas flow rates for column studies were measured at the outlet with a soap bubble flowmeter. Asbestos for gooch crucibles (BDH) was powdered and material of 100 mesh particle size was used. Deactivation of asbestos was done by the methanolic sodium hydroxide procedure[13]. Silicone oil (E. Merck) was coated on asbestos (20%) in an acetone bath using a rotary evaporator. The column was packed using a column filling jar and mechanical vibrator. The ends of the column were plugged with glass wool. For comparison, celite 545 was used after size grading to 100 mesh. Sterchamol was used as received. The packing of asbestos, as compared to sterchamol and celite, was more time consuming. Coated columns were conditioned overnight at the temperature of measurement. A mixture of six benzene derivatives containing equal volume of each was used.

Basis of intercomparison — The criteria for intercomparing column performance have been controversial. Dimbat *et al.*[3] compared the performance of celite and C.22 firebrick columns at identical temperatures, gas flow rates and packing ratios. Higher, values of resolution, lower pressure drop

and easier packing were considered important factors in deciding the suitability of a solid support. Frederick et al.[14] suggested that each column should be separately optimized for all the variables, such as temperature, particle size, packing ratio and carrier gas velocity. According to them, another important factor is the normalization of the analysis time. In the present study, a number of factors were optimized as discussed below.

The gas flow rate was optimized for asbestos-silicone column at different temperatures. The performance of sterchamol and celite columns was compared under these optimized conditions. A similar approach was adopted by Sawyer and Barr[15] for the evaluation of support materials, namely chromosorb W, glass beads, nichrome beads, carborundum and fluoropak. Thus the height of equivalent theoretical plate (HETP) for benzene was determined at a definite temperature as a function of gas flow rate. From these Van Deemter plots of asbestos-silicone column, the optimum gas flow rate for the minimum value of HETP was determined.

The choice of particle size of the solid support has been studied by many workers[4,16,17]. The general conclusion was that higher resolution was obtained with smaller particle size solid supports. Keeping this in view asbestos and celite were size graded to 100 mesh, whereas sterchamol was used as received. It was assumed that the original size of sterchamol solid support was optimum.

In this study, silicone oil (E. Merck) was used as the stationary phase for all the columns, thus fixing one of the experimental variables. In a preliminary study, it was found that the variation of liquid loading on asbestos from 1-20% (by wt) resulted in a constant value for the retention volume of benzene. As there seems to be no adsorption at these loadings, the upper limit, i.e. 20%, was used in the case of all the three columns. However, in the case of diatomite treated glass beads, Kirkland[8] observed that thinner liquid loadings yielded lower HETP and efficient solute mass transfer.

For column comparison, optimization of time was also done, as it is always desirable to reduce the retention times for selecting the best solid support. Thus, for the 1 m column, the best solid support was defined as that which gave the highest value of resolution for a particular pair within an analysis time of 10 min.

However, optimization of every variable for each column multiplies the amount of experimental work enormously without achieving a proportionate gain in the validity of conclusions. We have assumed that optimizations done by us will enable reasonably valid conclusions to be arrived at.

Results and discussion

The physical properties of the solid support used were as follows: Density, 0·27 g/ml; particle size, 100 mesh; permeability, $0·31 \times 10^{-7}$ sq cm; porosity, 0·42; and sp. surface area, 120 sq m/g.

The Van Deemter plots for 1 m asbestos-silicone column at 100°, 125° and 150°C, gave the minimum HETP at the gas flow rates of 75, 39 and 28 ml/min respectively. The chromatograms obtained under these conditions are shown in Fig. 1 (A-C). The performance of the asbestos column was compared with those of celite 545 and sterchamol for 1 m long columns. Data on relative retention volumes with respect to benzene in 1, 2 and 3 m absestos-silicone columns are given in Table 1. Fig. 2 depicts a chromatogram for a 3 m column. Comparative values of resolution and separation factors for each pair in the mixture for the asbestos column are given in Table 2. Comparative data indicative of the performance of columns of asbestos, celite 545 and sterchamol columns are given in Table 3.

Data given in Table 1 show that with increase in temperature from 100° to 150°C, the relative retention volumes of all the components with respect to benzene go on decreasing in all the asbestos-silicone oil columns. It was also observed that the values of relative retention volumes of different components in the asbestos column

were midway between the values in celite and sterchamol columns, the values being higher in sterchamol. This implies that the retention times in the asbestos column are lower than the retention times in sterchamol column.

It is evident from the results given in Table 2 that the separation factor and resolution of all pairs in the mixture increase on increasing asbestos column length at all the three temperatures. Highest values were obtained at 100°C (Fig. 1A). The number of theoretical plates in the asbestos column increased with increase in temperature and column length. Maximum number of theoretical plates was obtained for the 3 m column at 150°C (Fig. 2). Thus, the overall performance of this column was better.

Comparison of column performance using asbestos, celite 545 and sterchamol as solid supports in 1 m columns revealed that at 100° and 125°C, the resolution was of the same order with all the three solid supports,

Table 1 — Relative retention volumes of different solvents in asbestos-silicone oil columns of different lengths

(The values represent relative retention volumes with respect to benzene)

Temp. °C	Gas flow rate ml/min	Column length m	Toluene	p-Xylene	Bromo-benzene	o-Dichloro-benzene	Nitro-benzene
150	28	1	1·41	2·00	2·70	4·32	6·00
150	28	2	1·37	1·92	2·72	4·24	5·78
150	28	3	1·37	2·04	3·00	4·89	6·86
125	39	1	1·50	2·82	3·62	6·24	9·22
125	39	2	1·62	2·60	3·88	6·15	9·12
125	39	3	1·50	2·34	2·53	5·95	8·68
100	75	1	1·90	3·30	5·40	9·90	15·60
100	75	2	1·95	3·80	6·30	10·80	16·62
100	75	3	1·82	3·30	5·55	10·70	16·10
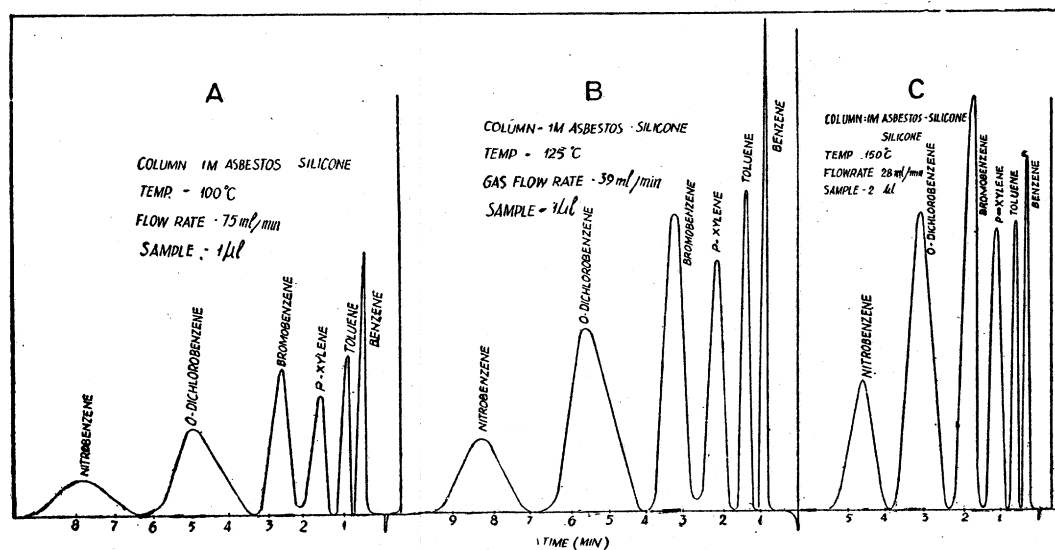
Fig. 1 — Chromatograms showing separation of hydrocarbons under different conditions using a 1 m column

COLUMN: 3M ASBESTOS-SILICONE
TEMP. - 150 °C
FLOW RATE - 28 ml/min
SAMPLE - 2 μl

NITROBENZENE · O-DICHLOROBENZENE · BROMOBENZENE · P-XYLENE · TOLUENE · BENZENE
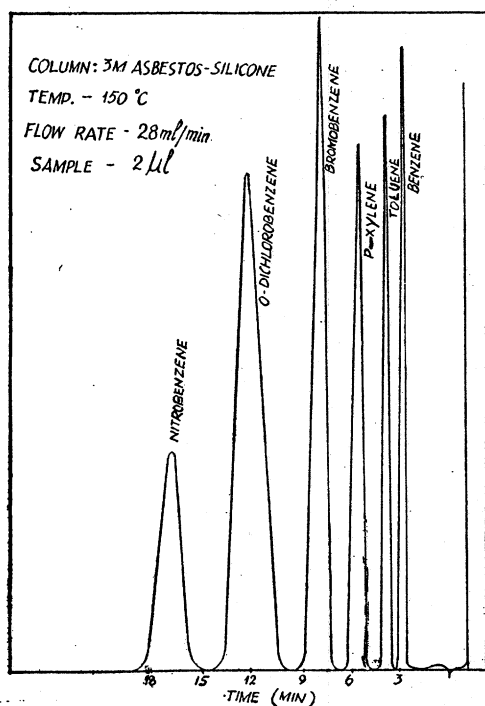
TIME (MIN)   15   12   9   6   3

Fig. 2 — Chromatogram showing separation of hydrocarbons on a 3 m column

whereas at 100°C, sterchamol effected comparatively greater resolution than others (Table 3). The separation factor, however, was highest in asbestos column at 100°C. At other temperatures, the separation factor was higher in asbestos and sterchamol than in celite. The number of theoretical plates was highest in the celite column. In asbestos, the maximum number of theoretical plates (180) was obtained at 150°C, whereas in the case of celite, the maximum value (226) was obtained at 125°C. In sterchamol, the number of theoretical plates was minimum. Comparing the columns for analysis time, it was observed that sterchamol took longer time at the same temperature and gas flow rates as compared to celite and asbestos. Within an analysis time of 10 min, the highest values of resolution were comparable at 100°C for asbestos and celite. For asbestos and celite the resolution values were 1·12 and 1·13 and the analysis times 9·50 and 5·75 min respectively. Thus celite

Table 2 — Relative values of resolution (R) and separation factors (S) for different solvent mixtures in asbestos-silicone oil columns

Temp. °C	Gas flow rate ml/min	Column length m	No. of theoretical plates	Benzene-toluene		Toluene-p-xylene		p-Xylene-bromobenzene		Bromobenzene-o-dichlorobenzene		o-Dichlorobenzene-nitrobenzene	
				R	S	R	S	R	S	R	S	R	S
150	28	1	180	1·01	1·41	0·92	1·42	0·93	1·35	1·08	1·60	0·90	1·40
150	28	2	215	1·06	1·37	1·00	1·41	1·03	1·42	1·10	1·54	0·95	1·38
150	28	3	360	1·09	1·26	1·08	1·38	1·22	1·40	1·38	1·50	1·19	1·36
125	39	1	82	1·07	1·50	1·00	1·69	0·93	1·51	1·10	1·72	0·91	1·48
125	39	2	164	1·14	1·68	1·14	1·58	1·30	1·49	1·27	1·60	1·22	1·48
125	39	3	256	1·80	1·50	1·67	1·56	1·50	1·50	1·91	1·70	1·50	1·46
100	75	1	54	1·12	1·90	1·09	1·72	0·99	1·65	1·19	1·83	0·94	1·57
100	75	2	88	1·28	1·85	1·46	1·94	1·39	1·67	1·61	1·82	1·62	1·62
100	75	3	122	1·86	1·82	1·87	1·85	1·61	1·65	2·03	1·93	2·55	1·50

Table 3 — Relative performance of columns using asbestos, celite 545 and sterchamol solid supports

(Length of column, 1 m)

	Asbestos			Celite 545			Sterchamol		
Temp., °C	150	125	100	150	125	100	150	125	100
Gas flow rate, ml/min	28	39	75	28	39	75	28	39	75
Resolution*	1·01	1·07	1·12	1·01	1·06	1·13	1·00	1·00	1·55
Separation factor*	1·41	1·50	1·90	1·37	1·33	1·70	1·46	1·71	1·87
No. of theoretical plates†	180	82	54	72	226	177	67	46	51
Analysis time, min	5·50	9·75	9·50	3·80	5·00	5·75	11·20	17·25	24·50

*For benzene-toluene.
†For benzene peak.

may be taken to be a slightly better solid support than asbestos. At 150°C, the analysis time was reduced to 5·50 min in the asbestos column, but then there was a fall in resolution to 1·01. Comparison of resolution, separation factor, retention times and number of theoretical plates of other components and pairs in the mixture also leads to similar conclusions. Asbestos, therefore, seems to compare well with celite and to be superior to sterchamol as a solid support.

The importance of large surface area for good separations in the case of porous supports has been recognized[18]. Saha and Giddings[19], who compared the performance of chromosorbs P, W, G and gas chrome S ascribed the superiority of chromosorb P to its very fine pore structure. The high porosity and large surface area of asbestos column seem to reduce the analysis time significantly. The absence of tailing in the chromatograms suggests that a larger specific surface area does not lead to detrimental adsorption effects.

Recently there has been a growing trend to reduce the retention times in gas chromatographic analysis. Most of the methods so far employed accomplish this by increasing the column temperature, increasing the carrier gas velocity, dereasing the packing ratio, decreasing the length of the column and choosing a liquid phase which results in smaller partition coefficients. But no attention has been paid to the nature of the solid support used. It seems that the solid support also plays an important role, and in most cases, the changing of the solid support, e.g. asbestos, may affect this reduction considerably. Although the solid support in gas liquid chromatography is commonly thought to be an inert material in the separation process, many workers[16,19-25] have contradicted this and have indicated that there is every possibility of an interaction between the solute and the support material. The present study also makes it increasingly evident that the choice of the solid support in gas liquid chromatography is also an important factor and the possibility of solute-solid support interaction cannot be ruled out. Further work on the use of asbestos for the separation of other compounds and on the elucidation of the nature of solute-solid support interaction is in progress.

Acknowledgement

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